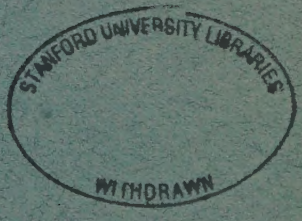
Sulfuryl Chloride Manufacture and Uses

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK

By

CARROLL M. SALLS, B.S.



NEW YORK, N. Y.
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Sulfuryl Chloride

I—Principles of Manufacture from Liquid Sulfur Dioxide

Sulfuryl chloride has been one of the medium priced chemicals, but one which, if the cost were cheap enough, would have a much more extensive use.

Basing their work on the modern theories of contact catalysis, the authors have worked out a new method for the manufacture of sulfuryl chloride which promises to place this chemical industrially in the "heavy chemical market" class. Over 99 per cent yield of 98 per cent purity sulfuryl chloride is obtained by direct combination at room temperature in iron apparatus of pure sulfur dioxide and chlorine, and removal of the catalyst by filtration.

NEW uses for any article of commerce are naturally of interest to manufacturers of that article. When the article happens to be a by-product or a waste product, the question of uses assumes greater importance. In some cases where uses have been found for a by-product, the whole process has been stimulated to greater production because part of the profits realized on the by-product have been applied for the purpose of underbidding competitors on the principal product. Competition eventually eliminates profit, but as that state of equilibrium is approached the cost of the principal product is decreased to such a degree that entirely new fields of technology may be opened up in which the principal product can be applied.

Sulfur dioxide and chlorine are both by-products of large-scale operations and, in addition, their toxic action makes it difficult to throw either material away even when that is economically possible. Consequently, a simple method of combining these two materials to make a useful product should be of interest to producers of both materials.

Brallier[1] has recently expressed the urgent need of finding new tonnage uses for chlorine. Over one-half of the installed capacity of the country is lying idle and there is no prospect of utilizing more than a small fraction of this idle equipment. After a review of the production statistics for chlorine products and analysis of possible outlets for chlorine, this author ex-

[1] *Chem. Met. Eng.*, **28**, 846 (1923).

presses the opinion that manufacturers of chlorine should make a coöperative effort to develop products that will provide some return on the millions of dollars of capital now invested in chlorine plants. Such constructive and united action has certain undeniable advantages in the direction of education of consumers, and it might lead to the building up of consuming capacity to the present producing capacity, or even further.

As for sulfur dioxide, the Chandler Lecturer for 1923[3] at Columbia University brought out very forcibly the reasons for the endless litigation directed against smelter operators by the pooled agrarian interests of the community. One large smelter discharged daily through a single tall stack several thousand tons of sulfur dioxide gas among other waste products. Sulfur dioxide from smelting operations of this kind has injured vegetation for miles around and polluted the air of nearby towns. Consequently, it has been profitable to wash a part of the stack gases and sell the sulfur dioxide in the form of liquid for the cost of recovery. One smelter (Tacoma, Wash.) has sold liquid sulfur dioxide to paper manufacturers at $12.00 a ton.

It is true that combination with chlorine could at best utilize only a small part of this sulfur dioxide, but it might at least mitigate the nuisance of one of the smaller smelters to such a degree as to satisfy the demands of the community.

The writers' investigation has developed a method for the manufacture of sulfuryl chloride which they believe to be much cheaper than methods hitherto used, possibly cheap enough to permit the manufacture of sulfuric acid and hydrochloric acid from it by the addition of water.

When produced at this cost, a long list of applications of this remarkably active chemical would be opened up. Sulfuryl chloride is a vigorous chlorination agent, producing in general—not always—the same products as elementary chlorine. It will be shown in a subsequent article that it is especially applicable in gaseous reactions such as the chlorination of methane, because the reacting mixture cannot explode and undesirable reactions are much more easily controlled. The use of sulfuryl chloride in the manufacture of acetic anhydride has the advantages of forming less chloracetic acid, of supplying exactly the molecular proportions required by the reaction, of eliminating the necessity of removing free sulfur from the product, and of a price differential due to the fact that one of the present processes uses liquid sulfur dioxide and liquid chlorine whereas sulfuryl chloride can be produced, if desired, by the combination of sulfur burner gas with the chlorine as it leaves the electrolytic alkali cells. Chlorosulfonic acid—a material for which there is some demand—can be readily made directly from sulfuryl chloride. Like sulfur chloride, S_2Cl_2, sulfuryl chloride, SO_2Cl_2, vulcanizes rubber; but as yet no method of con-

[3] Swain, *Ind. Eng. Chem.*, **15**, 296 (1923).

trolling the action to avoid the production of a brittle product has been found. The literature describes many other potentially valuable reactions of sulfuryl chloride, but the few applications mentioned here show sufficiently well that a cheap method for the manufacture of sulfuryl chloride will be instrumental in finding a use for some of the idle chlorine equipment of the country.

Old Processes

Sulfuryl chloride has been prepared by bringing sulfur dioxide and chlorine together in the presence of ethylene,[3] camphor,[4] acetic anhydride,[5] and many other organic compounds such as esters, terpenes,[6] formic acid, glacial acetic acid, charcoal,[7] etc. It is formed slowly when a mixture of chlorine and sulfur dioxide is exposed to sunlight, and more easily by heating chlorosulfonic acid in the presence of a catalyst.[8] It is commonly prepared technically by adding liquid chlorine gradually to liquid sulfur dioxide in which camphor has been dissolved.[9] Pope[10] makes the charcoal method continuous by passing equimolecular proportions of chlorine and sulfur dioxide into a reaction chamber packed with chunks of charcoal, but the method is not one that lends itself to production on a manufacturing scale. The sulfuryl chloride is drained off the bottom or removed as a vapor. Pope says, "due to the low thermal conductivity, it is difficult to maintain a uniform temperature throughout the catalyst in the mass of which the reaction is taking place." This matter is important because the yield of sulfuryl chloride decreases rapidly with rise of temperature. Moreover, in the operation of the Pope patent it is necessary to use equimolecular proportions of the reacting gases.

New Process

Sulfur dioxide and chlorine are continuously dissolved in a body of liquid sulfuryl chloride which carries activated carbon in suspension. When the reacting substances are nearly pure, the combination takes place rapidly and completely at room temperature. The carbon catalyst effects the combination of the dissolved substances, thus producing fresh solvent. Sulfuryl chloride is removed from the carbon by filtration, and the liquid is run directly into iron drums for shipment. Measurement of gases is avoided by the use of a volume of sulfuryl chloride sufficiently large to dissolve the total supply of either gas for several hours if neces-

[3] Regnault, *Ann. chim. phys.*, **69**, 170 (1838).
[4] Schultze, *J. prakt. Chem.*, **24**, 168 (1881).
[5] Aktien-Gesellschaft f. Anilin Fabrik, German Patent 226,218 (1909).
[6] Durrans, British Patent 124,542 (1918).
[7] Melsens, *Compt. rend.*, **76**, 9204 (1873).
[8] Wohl and Ruff, *Ber.*, **34**, 3509 (1901); German Patent 129,862 (1902).
[9] Badische, German Patent 138,531 (1901).
[10] Pope, British Patent 122,516 (1918).

sary. When dilute gases are used, it is preferable to reduce the vapor pressure of the sulfuryl chloride in the catalyzing chamber by cooling to 0° C. or by adding a solvent. Sulfuryl chloride vapors are removed from the exit gases by absorption in a solvent such as chlorosulfonic acid or pentachlorethane.

Since the carbon effects the reaction by virtue of selective surface action, it is obvious that the process is subject to the ills that attend contact catalysis. It is therefore important to point out as clearly as possible the action of the catalyst under the conditions of this process. The writers have succeeded in defining the peculiar conditions that govern the selection and use of a catalyst having a high activity and a long life.

Catalysis by Active Carbon

Within the past few years several types of highly activated carbon have been put on the market at a reasonable price. It has been known since 1873 that charcoal will catalyze the reaction between sulfur dioxide and chlorine, but in view of Trautz'[11] statements that coconut charcoal has almost no action and that two hundred and seventy out of three hundred experiments with animal charcoal had to be rejected, it was not at all certain that these highly activated carbons would be suitable for a commercial process. Behrend[12] reported a very poor yield when charcoal is used as the catalyst, and decidedly preferred the chlorosulfonic acid method. Apparently, there is some fundamental difference in the several types of carbon other than extension of surface which affects their catalytic activity. It seems to be the opinion of those who have had experience with this reaction that the camphor or the chlorosulfonic acid methods are the best. The first method, however, requires two distillations to produce a pure product, and there is a large loss of camphor due to reaction with sulfuryl chloride and sulfuric acid at the temperature required for distillation. The second method does not use elementary chlorine. A thorough study of the fundamental characteristics of the reaction in the presence of carbon has led the writers to disagree with this prior opinion.

Chlorine and sulfur dioxide are quite soluble in liquid sulfuryl chloride.[13] If carbon is added to a saturated solution of chlorine in sulfuryl chloride, the saturation disappears and the temperature of the liquid increases slightly. The liquid is now capable of dissolving more gas. The dissolved chlorine has been adsorbed by the carbon in a manner similar to the adsorption of acetic acid from aqueous solution. The same thing happens in a saturated solution of sulfur dioxide in sulfuryl chloride. If the carbon contains other gases, such as oxygen, nitrogen, carbon dioxide, or hydrogen chloride,

[11] *Z. Elektrochem.*, **14**, 534 (1908).
[12] *J. prakt. Chem.*, [2] **15**, 23 (1877).
[13] Schultze, *Ibid.*, [2] **24**, 176 (1881).

they are almost completely displaced when brought in contact with either chlorine or sulfur dioxide. Hence this is an example of selective adsorption. The greater part of the foreign gas is displaced immediately, but the last part is displaced more slowly. The concentration of foreign gas above the carbon must be decreased to a very small value before the last trace is removed.

If sulfuryl chloride is saturated with chlorine and sulfur dioxide in equimolecular proportions and carbon is added, the saturation disappears as before; but in this case it is not possible to saturate the liquid again by slowly passing in chlorine and sulfur dioxide in equimolecular proportions. The solute reacts to produce the solvent. This process goes on indefinitely and the number of grams of carbon per cubic centimeter of solvent continuously decreases, but the velocity of reaction remains constant provided that the concentration of dissolved gases stays constant and that the carbon surfaces remain intact. Consequently, the carbon has appeared in the role of a catalyst.

It may be possible to learn a little more about contact catalysis from this rather novel system. Such information would be of first importance to the writers, not in order to aid in the development of a general theory of catalysis by comparing their results with those of others, but to find out which theory of catalysis best explains the characteristics of this particular reaction. Then the facts that have been gathered around this theory will be more likely to aid in establishing the conditions necessary for the most economical operation of the process.

Faraday's conclusion[14] concerning the combination of gases in the presence of platinum, stated in modern language, is: Two reacting gases are absorbed by the platinum and, being thus brought into intimate contact with each other, proceed to react. Thomson[15] has shown that the surface tension of the absorbed film changes as the chemical reaction proceeds. The physical state of the catalyst itself changes during the reaction. Crystalline manganese dioxide used as a catalyst for the potassium chlorate decomposition becomes amorphous.[16] Clean platinum gauze used as a catalyst in the oxidation of ammonia becomes covered with a spongy deposit. Finely divided metals for hydrogenation change[17] their surface structure. These examples show that there is an interchange of energy between the catalyst and the reacting substances. Consequently, in the case of carbon it is probable that the energy which appears at the surface due to fine subdivision leaves the surface, is added to the driving force of the reaction, and returns to the catalyst when its

[14] Experimental Researches, Sixth Series, Vol. I, p. 165; also paragraph 361.

[15] "Application of Dynamics to Physics and Chemistry," 1888, pp. 206 and 236.

[16] Sodeau, *J. Chem. Soc.* (*London*), **77**, 137, 717 (1900); **79**, 247, 939 (1901); **81**, 1066 (1902).

[17] Sabatier, "La catalyse en chimie organique," 1913, p. 55.

work is done. This energy would appear as the excess of heat of absorption over heat of compression when there is no substance present with which the absorbed film can react. When a reaction takes place the energy would be returned to the catalyst by release of the product from the high pressure existing in the absorbed film.

Without committal concerning the mechanism of catalysis, we may, for the present, consider a positive catalyst as a substance that is capable of delivering a certain amount of energy per unit of time, and apply it in the same place and in the same direction as the energy that tends to drive the chemical reaction, thus causing an increase in the velocity of the chemical reaction. The mechanism may consist in the formation of intermediate chemical or other compounds, but that is not essential to such a conception of catalytic activity.

A chemical reaction results in a change of spatial relations through the application of forces associated with the constituent particles, the work balance usually appearing as the heat of reaction. The introduction of a time factor gives power. Hence catalytic activity has the dimensions of power.

In general, a small quantity of catalyst is sufficient to act upon a very large quantity of the reacting substances, but the *rate* at which the reacting substances will be converted does depend on the quantity of catalyst present. A definite quantity of catalyst can supply a certain maximum impulse and no more. The increase in the rate of hydrolysis of methyl acetate by increasing quantities of acetic acid is the best known example of this fact. A change in the extent and character of contact surfaces is known to affect the efficiency of the catalyst in heterogeneous systems.

The impulse supplied to a mixture of chlorine and sulfur dioxide by a unit weight of carbon is much smaller than is ordinarily the case with metallic catalysts—i. e., a comparatively large weight of carbon must be used to produce the same number of pounds of product per hour. One gram of the best carbon working at full capacity will produce 0.5 pound of sulfuryl chloride per hour, whereas 1 gram of platinum will produce several hundred pounds of sulfur trioxide per hour. The necessity for using this comparatively large quantity of catalyst makes it possible to subject the catalyst to ordinary quantitative manipulations such as purification and weighing with a percentage accuracy of the same magnitude as the rest of the experiment, and still keep within the limits of laboratory apparatus in measurements on the product and on the gases which go to make the product. The measurement of the maximum impulse imparted by several types of adsorbent carbon is described below. The fact that the reaction proceeds at a very slow rate in the absence of carbon makes it possible to stop the reaction at any time by a simple filtration through paper. The data on relative carbon activity supply a standard upon which to base calculations concerning the probable cost for catalyst,

capacity per unit volume of reaction chamber space, and the yield of sulfuryl chloride.

Relative Carbon Activity

A saturated solution of chlorine and sulfur dioxide in sulfuryl chloride at 25° C. contains 5 per cent of dissolved gases. At equilibrium at 25° C. sulfuryl chloride contains 1 per cent of dissolved sulfur dioxide and chlorine. Unsaturated sulfuryl chloride dissolves chlorine and sulfur dioxide at a rate far above the capacity of the meters used by the writers.[18] Carbon adsorbs chlorine and sulfur dioxide from a saturated solution very rapidly, but by working with a small sample of carbon it is possible to supply the gases at such a rate that the vapor pressure of the liquid remains at 760 mm.—i. e., the liquid remains saturated. Then the meter readings give directly the rate at which a known weight of carbon is producing a combination of chlorine and sulfur dioxide at any instant.

Although the chlorine and sulfur dioxide gases taken from cylinders were further dried by sulfuric acid and by passing through a tube containing phosphorus pentoxide on glass beads, it was found that the catalytic activity of the carbon gradually decreases, probably due to amounts of impurities too small for detection by the ordinary methods of gas analysis. It may be due to a change in the physical constitution of the catalyst itself, but this is improbable as the carbon can be reactivated by a simple washing and drying.

In order to determine the relative activity of several types of activated carbon, a series of experiments with each carbon was carried out in which the rate of supply of the gases was constant and the weight of carbon changed until the smallest weight was found that would cause the vapor pressure of the solution to remain below 760 mm. for 1 hour. Comparison of the minimum weights of carbon required thus expresses the relative activity of these carbons with sufficient accuracy, considering the large differences that were found.

The chlorine and sulfur dioxide gases from the meters were mixed in equimolecular proportions and passed into a 500-cc. flask immersed in a thermostat at 20° C. The flask contained the same quantity of redistilled sulfuryl chloride in each experiment. The sample of dry carbon was suspended in the sulfuryl chloride. The gas mixture was admitted to the flask through a 3-mm. (1/8 inch) i. d. glass tube at a constant rate of 147 liters per hour equivalent to 453 grams (1 pound) of sulfuryl chloride per hour. This made the linear velocity through the inlet tube 51.5 meters per second. The gases were completely absorbed—i. e., the yield of sulfuryl chloride was approximately 100 per cent of theory. In fact, a slight suction persisted in the outlet tube during the

[18] Benton, *Ind. Eng. Chem.*, **11**, 623 (1919); Arndt, "Handbuch der physikalisch, chemischen Technik," **1915**, p. 230; Oberfell and Mase, *Ind. Eng. Chem.*, **11**, 294 (1919).

greater part of the experiment. In the absence of a catalyst the amount of liquid taken for each experiment would be, at this rate, saturated with the gas mixture in 2 minutes. Then the gas mixture would come through the liquid unchanged. The gases rising part way through the liquid produced a vigorous agitation. Since the number of grams sulfuryl chloride formed per minute was constant, thermometers inside and outside of the flask showed nearly a constant temperature difference of 10° C.

The minimum weight of catalyst required to bring 453 grams (1 pound) per hour of an equimolecular mixture of chlorine and sulfur dioxide to equilibrium is given in Table I.

Silica gel does not catalyze the reaction between dry chlorine and sulfur dioxide. It adsorbs a gas by virtue of capillary attraction only, and therefore the adsorbed film does not make effective contact with the surface. The energy cannot leave the surface.

TABLE I

	Grams
Norit	1.8
Darco	2
McKee carbon	8
Filtchar	15
Blood charcoal	25
Camphor	30
Animal charcoal	70
Coconut charcoal	75
Whetlerite	90
Batchite	110
Oak charcoal	140
Birch charcoal	160
Nitrobenzene	600
Silica gel	20,000 (or more)

Inspection of the table shows that those carbons that are capable of delivering a relatively large impulse are all decolorizing carbons, and that acid-treated carbons are more active than alkaline carbons. When the energy exists on the surface of the carbon in the form of a positive charge, there is apparently a greater acceleration of the reaction between negative radicals.

The highly activated carbons that were developed during the war for the purpose of absorbing gases were found to possess comparatively small catalytic activity for this reaction. Decolorizing carbons such as Norit and Darco have about forty times as great activity as a good coconut charcoal obtained from the Edgewood Arsenal. This coconut charcoal had a 40-minute chloropicrin activity, accelerated test. Whetlerite, a copper-impregnated charcoal, had a 30-minute activity, accelerated test.

The great difference between the catalytic activity of gas carbons and decolorizing carbons can be explained on the basis of diameter and length of capillaries. The uncombined chlorine and sulfur dioxide must diffuse through the sulfuryl chloride that fills the capillaries in order to reach the catalyzing surface, where combination takes place rapidly and a corresponding amount of sulfuryl chloride is pushed out of the capillary. When the capillary is long and narrow,

as in gas carbons, the solute diffuses to the walls before it can penetrate very far. Hence the bottom of the capillary must be filled with pure sulfuryl chloride and the concentration of solute continuously increases as the entrance is approached. The result is that only the carbon near the entrance of the capillary is exerting its catalytic action. A fish-scale structure, on the other hand, as claimed for Darco carbon, offers much less opportunity for long capillaries, and consequently a much larger proportion of the carbon is active.

The carbon is very easily separated from the sulfuryl chloride by filtration through paper. The sulfuryl chloride runs through faster than clear water. The filtrate is a light yellow, transparent liquid containing over 98 per cent SO_2Cl_2. The remainder is free chlorine and sulfur dioxide. This is pure enough for most purposes, but if a still purer product is desired the liquid may be distilled and the first 20 per cent of the distillate reworked. The remaining 80 per cent distils between 60° and 70° C. as a water-white distillate. There is no distillate above 70° C. The pure product may be distilled with less than 1 per cent loss, showing that sulfuryl chloride is a stable compound. No evidence of decomposition could be detected in several 8-pound bottles that had been standing for 2 years in diffused sunlight.

Catalyst Poisons

Moisture, sulfuric acid, chlorosulfonic acid, and nitrobenzene poison the catalyst. Carbon tetrachloride, pentachlorethane, tetrachlorethane, benzene, kerosene, etc., do not poison the catalyst. Moisture hydrolyzes some of the sulfuryl chloride, producing sulfuric acid, which forms a protective film over the surface of the carbon. A catalyst that has been poisoned by the addition of water can be completely regenerated by washing thoroughly with water and then drying in any suitable manner. Suitable methods of drying are: heating at 150° C. preferably *in vacuo;* heating to 500° C.; heating in a current of a dry gas such as hydrogen chloride, air, chlorine, sulfur dioxide, or carbon dioxide; washing with alcohol and ether. Absorption of moisture from the air can be prevented by saturation of the dried catalyst with chlorine. This also prevents scattering of the catalyst when sulfuryl chloride is added. Since a good grade of decolorizing carbon can be obtained for 7 cents a pound, it is probably advisable to throw the catalyst away when it becomes inactive. Table I shows the cost for catalyst should be less than 40 cents per ton of sulfuryl chloride.

Materials of Construction

Sulfuryl chloride has almost no action on iron at room temperature. The same applies as well to dry sulfur dioxide and dry chlorine. In the experimental work iron vessels in continuous service for months have shown almost no corrosion. Sulfuryl chloride is commonly shipped in ordinary sheet steel drums.

Cost of Operation

Simplicity, small capital investment, and flexibility of operation are the outstanding features of the equipment required for the manufacture of sulfuryl chloride from liquid sulfur dioxide. The total cost of operation, which includes the cost of the carbon at 7 cents a pound, water, steam, and air, labor at $5.00 a day, repairs, overhead, interest on investment at 6 per cent, and amortization over a period of 3 years, is estimated at about $10.00 per ton of sulfuryl chloride on a production of 10 tons of sulfuryl chloride per day. Taking 5 cents per pound as the cost of liquid sulfur dioxide in ton lots and 2.5 cents for chlorine as it comes from the cells, the cost of sulfuryl chloride by this new process should be less than 5 cents per pound.

If sulfuryl chloride is to be used to make hydrochloric acid, liquid sulfur dioxide is too expensive at the present time. In another paper the use of the cheap sulfur burner gas in the manufacture of sulfuryl chloride will be described.

II—Principles of Manufacture from Sulfur Burner Gas

In this method cheap, dilute gases are dried and brought into contact with active carbon of the proper type, and by cooling and use of absorbents the sulfuryl chloride is recovered for shipment. This is believed to be the first method that has been proposed which permits the use of dilute gases—e. g., 14 per cent sulfur dioxide—in the making of sulfuryl chloride.

IN AN earlier paper[1] a process for the manufacture of sulfuryl chloride from liquid sulfur dioxide was outlined. In order to make sulfuryl chloride available as an agent for the shipment of chlorine from chlorine works to markets for hydrochloric acid, it is necessary that sulfur dioxide be obtained at approximately the same cost as in the manufacture of sulfuric acid, because a salable sulfuric acid is a by-product from the manufacture of hydrochloric acid from sulfuryl chloride. In the present paper a process using a cheaper source of sulfur dioxide, such as a sulfur burner gas containing 14 per cent sulfur dioxide, will be described.

The two most important problems that appear when this dilute sulfur dioxide is substituted for concentrated sulfur dioxide are—first, the absorption of sulfuryl chloride vapors from the stream of inert gases; and second, the effect of temperature on the yield of sulfuryl chloride.

Absorption of Sulfuryl Chloride Vapors

An ideal absorbent for this purpose should not react with sulfuryl chloride nor introduce impurities that would render hydrochloric acid produced from it unfit for use in food products. It should have a low vapor pressure at the temperature of absorption. Chlorosulfonic acid, SO_2ClOH, meets these requirements. It is the intermediate product of the hydrolysis of sulfuryl chloride and at ordinary temperature has a vapor pressure lower than water.

A gas saturated with sulfuryl chloride at 20° C. contains 15 per cent sulfuryl chloride by volume. Chlorine will react with 14 per cent sulfur dioxide at 20° C. to produce a gas mixture approximately saturated with sulfuryl chloride,

[1] *Ind. Eng. Chem.*, **16**, 279 (1924).

since one volume of sulfur dioxide makes one volume of sulfuryl chloride vapor. The fact that the gas stream entering the absorbing tower is saturated permits a high concentration of sulfuryl chloride in the absorbent. In one experiment a mixture of 90 per cent sulfuryl chloride and 10 per cent chlorosulfonic acid at 20° C. was still absorbing sulfuryl chloride vapor from a gas stream carrying 15 per cent sulfuryl chloride. The heat losses in the fractionation of this mixture, therefore, will not be large.

The following experiment shows the action of the absorbent: Dry air at the rate of 187 liters (6.6 cubic feet) per hour was passed through 350 cc. of pure sulfuryl chloride in a 500-cc. graduate into 350 cc. of pure chlorosulfonic acid in a similar graduate. Both cylinders were immersed in a thermostat at 25° C. Folin absorbers were used as gas inlets. The excellent performance of these absorbers when used for the saturation of a gas with a vapor at rapid rates is shown by the

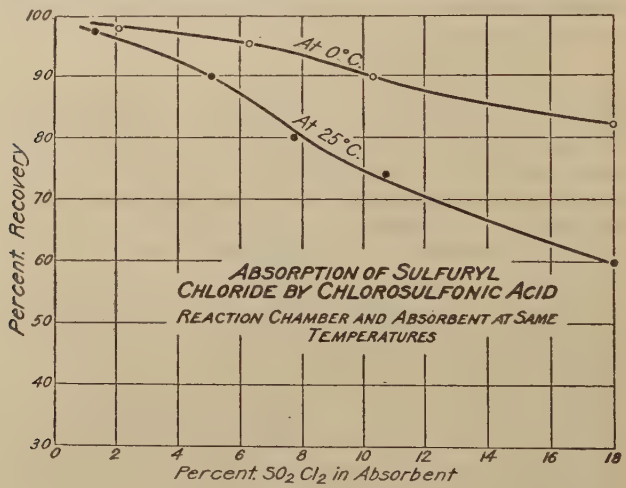


FIG. 1

fact that when the gas mixture issuing from the saturating vessel was passed through a coil condenser maintained at a temperature only 2 degrees lower than that of the saturator, drops of sulfuryl chloride liquid appeared at the end of the condenser in a few minutes. The completeness of absorption of sulfuryl chloride vapors from the gas stream is shown by the curves in Fig. 1, which define the conditions for equilibrium between the gas and liquid phases at different points in the absorption tower. The percentage recovery obtained by dividing the gain in weight of absorbent by the loss in weight of sulfuryl chloride is plotted against the concentration of sulfuryl chloride in the absorbent. Reading from the curves, a gas saturated with sulfuryl chloride vapor at 0° C. comes to equilibrium with an 18 per cent solution of sulfuryl chloride in chlorosulfonic acid when 82 per cent of the vapor has condensed. At 25° C. an 18 per cent solution will ab-

sorb 60 per cent and a 3 per cent solution 95 per cent of the vapor out of a gas mixture saturated with sulfuryl chloride at 25° C.

Yield of Sulfuryl Chloride

A mixture of chlorine and 14 per cent sulfur dioxide was passed through a body of liquid sulfuryl chloride in which carbon was suspended and the sulfuryl chloride vapor was removed from the exit gases by absorption in chlorosulfonic acid. It was found that when the temperature of the catalyst suspension was maintained at 25° C. the yield of sulfuryl chloride was only 70 per cent. The remainder was uncombined sulfur dioxide and chlorine. These substances are not

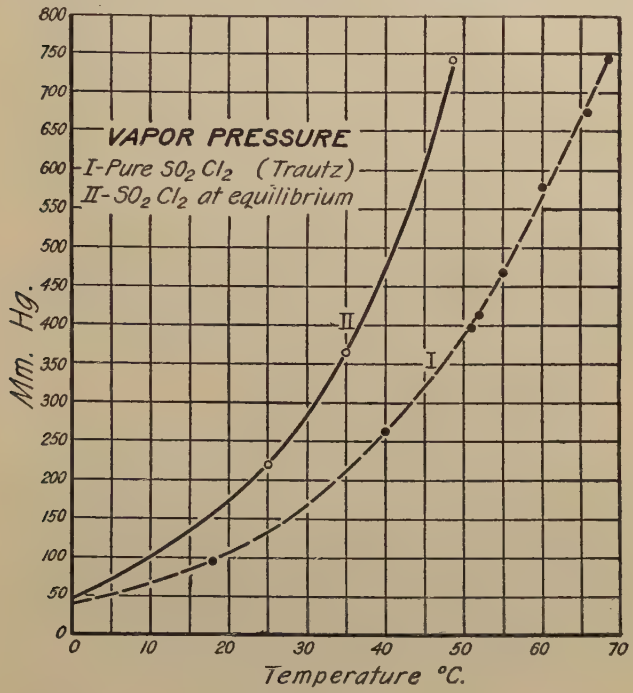


Fig. 2

very soluble in chlorosulfonic acid and consequently pass through unabsorbed. When the temperature of the catalyst suspension was lowered to 0° C. the yield jumped to 98 per cent.

The explanation is simple. The reaction

$$SO_2 + Cl_2 \rightleftarrows SO_2Cl_2$$

is reversible, and comes to equilibrium at 25° C. when 99 per cent of the sulfur dioxide and chlorine has been combined. The remaining 1 per cent dissolves in the liquid sulfuryl chloride, and the vapor pressure of the solution is considerably higher than that of the pure liquor as would be expected from Henry's law. When an inert gas is passed through the solution, the several components of the solution will be removed in

amounts proportional to the respective partial pressure which each component exerts. At 25° C. the vapor pressure of pure sulfuryl chloride is 142 mm., and of sulfuryl chloride containing carbon 205 mm. 142 divided by 205 is 69.7 per cent, which checks with the 70 per cent yield of sulfuryl chloride obtained by running the catalyzing chamber at 25° C.

It is evident that the yield can be increased by making the vapor pressure of the solution more nearly coincide with the partial pressure exerted by the sulfuryl chloride when pure. The curves of Fig. 2 show that the vapor pressure of sulfuryl chloride at equilibrium approaches the vapor pressure of pure sulfuryl chloride as the temperature is decreased. At 0° C. the respective vapor pressures are 40.9 mm. and 44 mm., or a ratio of 93 to 100. In addition to the increase in yield due to the approximation of the two vapor pressure curves at 0° C., there is a further increase in yield due to the comparatively low vapor pressure of sulfuryl chloride at 0° C. At 0° C., 70 per cent of the sulfuryl chloride vapor is condensed from a 14 per cent mixture. These two sources of improvement account for the 98 per cent yield obtained by running the catalyzing chamber at 0° C.

In a larger installation it may prove more economical to decrease the vapor pressure in the catalyzing chamber by the addition of a solvent, or by a combination of cooling and solvent action. It is evident that the substance added to the catalyzing chamber must not poison the catalyst. Pentachlorethane is a suitable solvent.

Drying of Gases

Several methods are available for removing moisture from the sulfur dioxide and chlorine before entering the catalyzing chamber. Probably the most suitable one is a preliminary drying of the separate gases with 66° Bé. sulfuric acid, followed by electrical precipitation of acid mist from the mixture of sulfur dioxide and chlorine. When the sulfur dioxide and chlorine are mixed, their combined action decomposes the moisture according to the equation.

$$SO_2 + Cl_2 + H_2O = H_2SO_4 + 2HCl$$

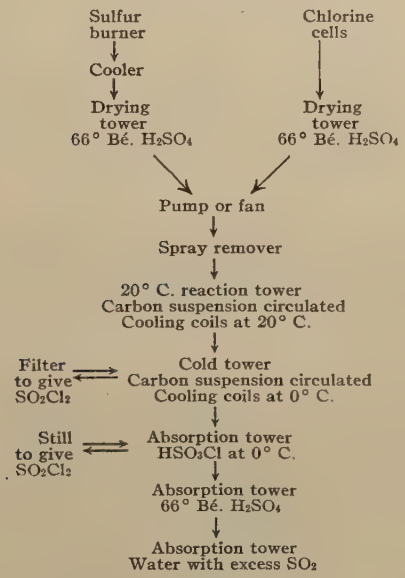
the sulfuric acid separating as a mist and the hydrogen chloride passing through the system as an inert gas. It is obvious that other methods of removing the moisture are available—e. g., reaction with sulfuryl chloride and adsorption of the sulfuric acid on carbon; reaction with chlorosulfonic acid made continuously by action of sulfuryl chloride on 100 per cent sulfuric acid containing a catalyst; and finally, reaction with oleum.

Refrigeration

Only a small amount of refrigeration is required, because most of the heat of reaction can be removed by cooling water. The catalyzing chamber is preferably divided in two parts, the first having cooling water coils and the second, brine

coils. Both low-temperature cooling water and the use of sulfur dioxide stronger than 14 per cent will decrease the cost for refrigeration, because more of the sulfuryl chloride will be condensed by the cooling water. An estimate of the maximum cost for refrigeration,[2] based on $1.25 per ton of ice and on the worst possible operation during a few weeks in the middle of the summer in West Virginia, with cooling water at 30° C. and using 14 per cent sulfur dioxide, shows a refrigeration cost of $1.00 per ton of sulfuryl chloride. A minimum estimate, based on a good operation for the winter months at Niagara Falls with cooling water at 10° C. and using 18 per cent sulfur dioxide, shows a refrigeration cost of 42 cents per ton of sulfuryl chloride. A conservative estimate of the refrigeration requirements for average operation is probably 75 cents per ton of sulfuryl chloride.

PROPOSED FLOW SHEET



The capacity of the catalyzing chamber should be considered in connection with the cooling system. The chemical reaction itself is very rapid. On the basis of one cooling system that the writers have operated on pure sulfur dioxide and chlorine, a catalyzing chamber of 1 cubic foot capacity would produce more than 1 ton of sulfuryl chloride per day. A catalyzing chamber should be designed more on the basis of heat to be removed and on the volume of gases to be handled than upon the rate of the chemical reaction.

[2] Marks, "Mechanical Engineers' Handbook," p. 1737, gives $2.00 as the cost for a ton of refrigeration delivered to consumers in cities, and approximately 50 per cent of this cost is the cost for power. At the lower cost for power prevailing at electrolytic alkali plants the cost of a ton of refrigeration should be less than $1.25.

Absorption System

The curves of Fig. 1 show that the percentage recovery of sulfuryl chloride from a gas stream issuing from a reaction chamber at 0° C. decreases much less rapidly when the temperature of the absorbent is 0° C. The divergence of the two curves would be a good deal more pronounced if the reaction chamber were at 0° C. and the absorbent at 25° C. Consequently, it is preferable to circulate the chlorosulfonic acid through this tower at approximately the same temperature as the cold tower.

The object of the absorption tower (indicated in the flow sheet) in which 66° Bé. sulfuric acid is circulated are—first, to absorb the small amounts of chlorosulfonic acid carried over from the first tower; and second, to produce continuously, if desirable, a fresh supply of chlorosulfonic acid. Sulfur trioxide in the form of oleum or as a solution in sulfuryl chloride can be run into this tower. The sulfur trioxide will react with the traces of dry hydrogen chloride in the exit gases to produce chlorosulfonic acid.

The object of the last tower is to absorb traces of hydrogen chloride, sulfuryl chloride, chlorine, and sulfur dioxide in order that a clean exit gas may be discharged into the atmosphere and any nuisance thereby avoided.

Material of Construction

While no experience has as yet been had with plant operations, yet from experience with small-scale operations, the writers feel that the following construction materials will serve well:

Towers should be of acid-resistant brick set in the customary acid-proof cement. Iron will serve for the coils, filter press, and other apparatus. The still for the distillation of the chlorosulfonic acid–sulfuryl chloride mixture should probably be of the type of the ordinary cast-iron nitric acid still, and the condensers should likewise be of one of the types customarily used for nitric acid. This still will be subject to some corrosion but the amount should not be excessive.

Cost Estimate

The total cost of operation, which includes carbon at 7 cents a pound, water, steam, air, repairs, refrigeration, labor at $5.00 per man per day, overhead, interest on investment at 6 per cent, and amortization over a period of three years, is estimated at $12.00 per ton of sulfuryl chloride on a production of 10 tons per day. Taking the cost of sulfur at $20.00, chlorine cell gas at $40.00, and a yield of 92 per cent, the cost of sulfuryl chloride by this process should be about $42.00 per ton.

III—Hydrolysis to Sulfuric and Hydrochloric Acids

If all the hydrochloric acid used in the United States were made from chlorine, 150 tons of chlorine per day would be required. In 1918 the liquid chlorine-producing capacity of the United States was 22 tons per day. The writers propose combining chlorine with sulfur dioxide and shipping the anhydrous liquid sulfuryl chloride in iron drums to the place where the hydrochloric acid is wanted and there adding steam to produce pure hydrogen chloride gas and 60 to 78 per cent sulfuric acid. The writers do not claim that this new process can compete in all localities with present processes, but there are some local conditions and special uses for which this process is especially adapted. The production of dry hydrogen chloride gas and dilute mixtures of sulfuric acid and hydrochloric acid are two special uses.

NEUMANN and Wilczewski have recently[1] published an exhaustive experimental study of the reaction

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

It is pointed out that the chemical change represented by this reaction can gain a new significance in Germany, because in the chlorine-alkali industry there has been a considerable excess of chlorine since the war. A Tobler tower[2] is recommended as suitable for producing concentrations of sulfuric acid the same as chamber or Glover acid (60 to 78 per cent). The sulfuric acid is practically free of chlorine and sulfur dioxide.

The simultaneous production of commercial hydrochloric and sulfuric acids has been proposed by other investigators. In 1903 Masson[3] patented a process for bringing chlorine, sulfur dioxide, and steam together in a heated chamber. Improvements on this process have been patented in Great

[1] *Z. angew. Chem.*, **36**, 377 (1923).
[2] U. S. Patent 1,332,581 (1920).
[3] French Patent 324,859 (1903).

Britain[4] and in Germany.[5] The last-named patent allows a mixture of chlorine and sulfur dioxide to meet with water, or better, hydrochloric acid flowing down in a reaction tower; at the bottom sulfuric acid of 65 to 80 per cent runs out and at the top gaseous hydrogen chloride escapes. It is stated that this process has given satisfactory results in practice, and that it can compete successfully with acids made in the ordinary way.

Coppodoro[6] gives a great deal of information concerning the process and includes estimates of costs. He recommends that the temperature in the apparatus should exceed 70° C. if over 70 per cent sulfuric acid is to be produced. Considerable heat (81.6 large Calories) is developed by the reaction. The process was in operation in 1909 in a plant at Ravenna, Italy. Welsh[10] uses electrical precipitation to remove sulfuric acid mist from the hydrogen chloride gas.

All these processes have two serious disadvantages. First, it is necessary carefully to regulate the proportions of chlorine and sulfur dioxide used. If there is an excess of either substance the large amount of inert gas from the sulfur burner would carry it straight through the absorption system, thereby causing a loss and creating a nuisance. Second, the expense of shipping hydrochloric acid away from the chlorine plant to the place where it is to be used quickly becomes prohibitive. To ship 1 ton of hydrogen chloride it is necessary to pay freight on 2.4 tons of water. The corrosive nature of hydrochloric acid adds greatly to the shipping cost. It is necessary to purchase and maintain expensive shipping containers, and to pay return freight on them.

These disadvantages would be eliminated by combining the sulfur dioxide and chlorine before the water is added. The preceding paper of this series[7] describes a low cost method for the manufacture of sulfuryl chloride from sulfur burner gas and chlorine. Sulfuryl chloride, SO_2Cl_2, is a liquid boiling at 70° C. and does not attack iron at ordinary temperatures. This anhydrous material could be shipped in iron drums to the place where hydrochloric is wanted and there water added to produce sulfuric acid and hydrochloric acid. This process has not yet been tried out in commercial apparatus. In the description of the experimental work it will appear that the following two reactions are chemically identical:

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$
$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

Hydrolysis at Ordinary Temperature

When sulfuryl chloride is added to an excess of water (1 volume to 10 volumes) at room temperature and the mixture is stirred, the reaction soon becomes so violent that

[4] Askenasy and Mugdan, British Patent 14,342 (1903).

[5] Consortium für electrochemischen Industrie, German Patents 157,043 and 157,044 (1902).

[6] *Gazz. chim. ital.*, **39**, 616 (1909).

[7] U. S. Patent 1,285,856 (1918).

the liquid mixture is forcibly expelled from the containing vessel.

The violent reaction is easily explained. Sulfuryl chloride is not miscible with water or with sulfuric acid, and is much heavier than water. It does, however, become cloudy when brought in contact with water, showing that a small quantity of water dissolves in the sulfuryl chloride. This water reacts to give sulfuric acid, hydrochloric acid, and heat. The sulfuric acid and the hydrogen chloride immediately take on water, generating more heat. The hydrogen chloride gas agitates the sulfuryl chloride, bringing a greater surface in contact with the water. The heat increases the reaction velocity. Soon enough heat is being liberated to boil the sulfuryl chloride, and these vapors coming in contact with the hot water cause still more favorable conditions for the hydrolysis. Then the reaction goes to completion in a few moments.

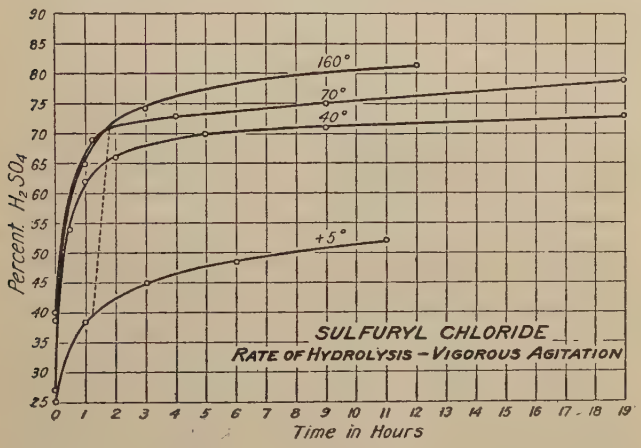


FIG. 1

If, however, the heat is removed so that the mixture is kept at room temperature and the mixture is not stirred, sulfuryl chloride will remain in contact with a large excess of water for several days. A layer of sulfuric acid is formed at the surface of the sulfuryl chloride and the reaction does not proceed until the sulfuric acid slowly diffuses into the water layer.

These two simple experiments indicate that the rate of hydrolysis of sulfuryl chloride decreases with increasing concentration of sulfuric acid in the aqueous layer.

HYDROLYSIS AT CONSTANT TEMPERATURES

This conclusion was tested out quantitatively by hydrolyzing sulfuryl chloride with a limited amount of water. Since it is known that at least a part of the water in a sulfuric acid solution exists as water of hydration, and furthermore, since it is known that hydrates of sulfuric acid are decomposed by a

rise in temperature, these experiments were carried out at four different temperatures.

A 200-cc. portion of water was stirred at a constant rate with an excess of sulfuryl chloride in a liter flask fitted with a reflux condenser and immersed in a thermostat at the specified temperatures. Analyses of the aqueous layer were made from time to time. The results are tabulated in Table I and plotted in Fig. 1.

Each of the curves shows an approximately constant rate of hydrolysis up to a certain concentration of sulfuric acid, and then another rate of hydrolysis—much slower—beyond that concentration. Furthermore, this change in the rate of hydrolysis occurs at a different concentration of sulfuric acid at different temperatures.

Dilute sulfuric acid is a solution of hydrated sulfuric acid in water. The writers believe that the sulfuryl chloride reacts with free water but not with the water of hydration. The curves indicate that in 72 per cent sulfuric acid at 70° C. nearly all the water is combined with the sulfuric acid as water of hydration. A decrease in temperature to 40° C. causes more water to combine with the sulfuric acid, so that nearly all the water in 65 per cent sulfuric acid at 40° C. exists as water of hydration. A still further decrease in temperature apparently brings the line of complete hydration (dotted line) at 5° C. to 39 per cent sulfuric acid.

TABLE I—HYDROLYSIS OF SULFURYL CHLORIDE AT VARIOUS TEMPERATURES

Time Hours	Specific Gravity at 17° C.	H_2SO_4 Per cent	HCl Per cent	Time Hours	Specific Gravity at 40° C.	H_2SO_4 Per cent	HCl Per cent
	At 5° C.				*At 40° C.*		
1	1.400	38.5	25.0	0	1.300	27	21.0
3	1.44	45.0	14.5	0.5	1.473	54	6.5
6	1.47	48.5	12.0	1	1.538	62	3.1
11	1.49	52.0	10.5	2	1.580	66	1.2
				5	1.615	70	0.6
				9	1.630	71	0.5
				19	1.650	73	0.17
	At 70° C.				*At 160° C.*		
0	1.335	40	11.5				
1.25	1.575	69	0.5	0	1.360	37	21.0
4	1.610	73	..	1	1.560	65	0.4
9	1.620	74	..	3	1.665	74	0.1
19	1.670	79	..	12	1.745	82	..

The fact that the hydrates of sulfuric acid are decomposed by rise in temperature indicates that in a solution of sulfuric acid there must be an equilibrium between the hydrates of sulfuric acid and free water. A hydrate of sulfuric acid will dissociate to give a lower hydrate and free water, and that lower hydrate will in turn dissociate to give a still lower hydrate and more free water. The concentration of free water in equilibrium with a highly hydrated sulfuric acid will be greater than that in equilibrium with a lower hydrate. This explains the shape of the curve obtained for hydrolysis at 5° C. The velocity of the hydrolysis reaction is proportional to the concentrations of the reacting components. As the concentration of free water decreases owing to its removal from solution by reaction with sulfuryl chloride the rate of hydrolysis gradually decreases. At the higher tem-

peratures there is a large concentration of free water in the solution, and the rate of hydrolysis is not appreciably affected until the point is approached where nearly all the water is held as water of hydration of the sulfuric acid. Beyond this point the concentration of free water in equilibrium with the hydrate is so small that the rate of hydrolysis is severely repressed.

Hydrolysis at Higher Temperatures

The boiling point of sulfuryl chloride is 70° C. In order to take advantage of the higher concentration of free water at higher temperatures, an experiment was carried out in the same apparatus at 160° C. The concentration of sulfuryl chloride when in the vapor phase is much lower than when in the liquid phase. The effect of this lower concentration of sulfuryl chloride can be detected in the curve, but its effect is much less important than the repression due to the low concentration of free water beyond the point of complete hydration.

The conclusion to be derived from these curves is that the most efficient commercial apparatus will be one in which the hydrolysis is carried out in the gas-liquid phase, the sulfuryl chloride and steam being in the gas phase and dilute sulfuric acid in the liquid phase. A simple tower with large internal surface would appear to be a satisfactory type of apparatus. The other factors, considered below, point to the same conclusion.

It is possible to make a strong sulfuric acid by simply allowing sulfuryl chloride to stand in contact with dilute sulfuric acid at room temperature. The longer time required is offset by the simplicity of the operation and by the fact that both reacting substances are in the liquid phase. If sufficient water is added to the sulfuryl chloride to dissolve all the hydrogen chloride, it is possible at room temperature to make a solution containing 35 per cent sulfuric acid, 25 per cent hydrochloric acid, and 40 per cent water. As soon as the solution becomes saturated with hydrochloric acid the hydrolysis proceeds more slowly. In one experiment water and sulfuryl chloride were allowed to stand together in a bottle at 40° C. The percentage sulfuric acid in the aqueous layer increased as follows: 1 day, 42 per cent; 3 days, 68 per cent; 7 days, 75 per cent; 12 days, 78 per cent; 3 months, 83.2 per cent.

For the production of pure acids, however, this type of operation is not recommended—first, because the sulfuric acid would have to be heated to drive out the sulfuryl chloride and hydrochloric acid; second, because the hydrogen chloride gas coming from the hydrolyzing vessel would carry along considerable quantities of sulfuryl chloride vapor; and third, because of the violence of the reaction in dilute solutions.

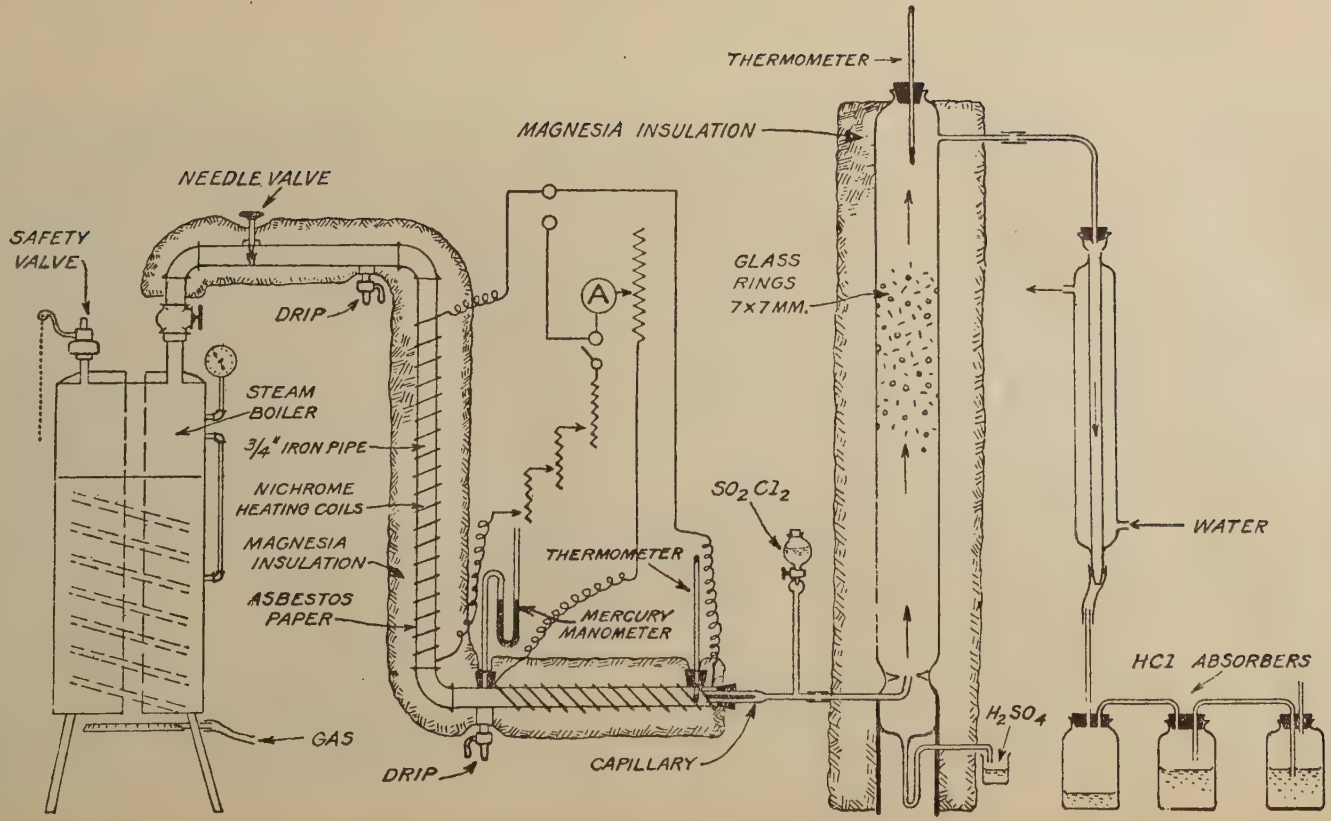


FIG. 2—HYDROLYSIS OF SULFURYL CHLORIDE

Hydrolysis in the Gas Phase

Dixon[8] observed that at 100° C. oxygen and sulfur dioxide do not combine in the presence of water vapor, although when a particle of liquid water is introduced into the system oxidation takes place at once. The hydrolysis of sulfuryl chloride also requires the addition of an oxygen atom to the sulfur dioxide group. The following experiment indicates that the hydrolysis of sulfuryl chloride has something in common with Dixon's observation:

An 8-mm. T tube was sealed to the top of a 3-liter, round-bottom Pyrex flask. Connections to a manometer and to a vacuum pump were sealed to one arm, and connections to burets containing sulfuryl chloride and water, respectively, were sealed to the other arm. The flask was immersed in an air bath at 160° C. After evacuation the flask was two-thirds filled with steam and the connecting tubes heated to prevent any condensation. Sulfuryl chloride vapor was then added to make a total of one atmosphere pressure, being very careful at all times to keep the temperature of this vapor above 130° C.

Contrary to expectation, there was no evidence of reaction. The manometer showed no pressure change. The inlet tube was then allowed to cool below 100° C. in order to condense a drop of water. Immediately the manometer pressure began to fall and drops of liquid condensed in the flask. The condensed liquid contained 74.3 per cent sulfuric acid and 0.8 per cent hydrochloric acid. Some unchanged sulfuryl chloride remained in the flask. Apparently the drop of liquid water had catalyzed the hydrolysis of sulfuryl chloride.

Heat of Reaction

A large amount of heat is generated by the hydrolysis of sulfuryl chloride. The combination of sulfuryl chloride vapor with steam to make 70 per cent sulfuric acid and hydrogen chloride gives out 67 large Calories per mol of sulfuryl chloride, or 890 B. t. u. per pound. This is one-fifteenth the calorific power of a good coal. Upon the assumption that no heat is lost by radiation, this quantity of heat is sufficient to concentrate all the 70 per cent sulfuric acid to 100 per cent, then to dissociate this sulfuric acid completely into sulfur trioxide and water, and finally to raise the temperature of the sulfur trioxide and hydrogen chloride to 430° C. The sulfur trioxide and hydrogen chloride could combine to make chlorosulfonic acid. Since chlorosulfonic acid reacts vigorously with the water of hydration in all strengths of sulfuric acid—even 95 per cent—it should therefore be possible to produce any strength of sulfuric acid up to 100 per cent. This very desirable result has not yet been realized experimentally. The writers have not yet been able to realize the condition of no radiation losses in an apparatus for hydrolyzing sulfuryl chloride by steam.

[8] *J. Gas Lighting*, **37**, 704 (1881).

Tower for Hydrolysis of Sulfuryl Chloride

A review of the foregoing results shows that a tower for the hydrolysis of sulfuryl chloride should be constructed in such a manner that the following conditions are efficiently met:

1—A large surface of contact between gas and liquid.
2—Constant relative motion at the interface of gas and liquid.
3—Absence of any stagnant areas in either gas or liquid.
4—Absence of any channels in the packed tower through which either gas or liquid can pass without adequate contact with the other phase.
5—A temperature high enough to obtain a sufficient concentration of free, liquid water in the circulating sulfuric acid.
6—Control of the violence of the reaction at the start.
7—Sufficient time for the completion of the reaction.
8—Removal of sulfuryl chloride and hydrochloric acid from the sulfuric acid.
9—Removal of sulfuryl chloride vapors and sulfuric acid mist from the hydrogen chloride gas.

A small tower which had satisfactorily reproduced the operating conditions and products that are realized in a commercial tower for the denitration[9] of waste acid was slightly modified to meet these requirements, and then used for the hydrolysis of sulfuryl chloride.

This laboratory denitrating column (Fig. 2) consisted of a 5.5-cm. Pyrex tube, 70 cm. long, with an inlet at the bottom for the mixture of sulfuryl chloride and steam, a trapped outlet at the bottom for sulfuric acid, a thermometer, and an outlet for hydrogen chloride at the top. The column was well insulated with magnesia. Steam under pressure was admitted through a needle valve into a superheater fitted with a mercury manometer and a petcock for removal of condensed water. Steam at 200° C. and atmospheric pressure passed through a 3-inch section of capillary tube in the end of the superheater. Sulfuryl chloride liquid was dropped into the superheated steam in the short section between the capillary tube and the column. The steam flow was measured by noting the manometer reading and was regulated by the needle valve. Winding the superheater with wire of high electrical resistance all the way from the needle valve to the capillary tube prevented condensation, and consequently a steady manometer reading could be obtained during the greater part of the experiment. The column was packed with rings 7×7 mm. which had 1-mm. walls and 71 per cent free space.[10] The cubic capacity of the column without packing was 1800 cc.; therefore the internal surface was 1.74 square meters.

Steam was passed through the tower until the thermometer at the top read 100° C. The sulfuryl chloride was then passed in and the rate increased until sulfuryl chloride began to appear at the exit. At a slightly lower rate than this the sulfuryl chloride was almost completely hydrolyzed. A small amount of sulfuryl chloride vapor in the hydrogen

[9] Pauling, U. S. Patent 1,031,864 (1912).
[10] Zeisberg, *Trans. Am. Inst. Chem. Eng.*, **14**, 321 (1922).

chloride can be detected by dissolving the hydrogen chloride in ice water. Oily drops of sulfuryl chloride appear in the ice water.

The gases issuing from the top of the tower contained hydrogen chloride and steam together with a small quantity of sulfuric acid mist. The temperature at the top of the tower was 106° to 112° C., and increasing the rate for sulfuryl chloride decreased this temperature. The rate of sulfuryl chloride addition was 65 grams per hour and a 25 per cent excess of steam at 200° C. and atmospheric pressure was used. The sulfuric acid running out of the bottom of the tower contained 58 per cent sulfuric acid and 0.38 per cent hydrochloric acid. The hydrochloric acid obtained by absorbing the exit gases after washing with a small quantity of water contained 33.58 per cent hydrochloric acid and 2.88 per cent sulfuric acid. The purity of the acids obtained in this experiment is therefore within the limits of purity of commercial acids produced in the ordinary way, but the improvements suggested below should remove all doubt as to the question of purity.

The data obtained on this small tower supply an experimental foundation for an opinion as to what may be reasonably expected from a large tower. Suppose that the Glover tower of a 25-ton chamber sulfuric acid plant were used for the hydrolysis of sulfuryl chloride. The dimensions of this tower would be about 7.3 by 3.66 meters (24 feet × 12 feet).[11] Assuming half the capacity per unit volume as obtained by the small denitrating column, this tower would hydrolyze 37 tons sulfuryl chloride per 24 hours, producing simultaneously 57 tons of 22° Bé. hydrochloric acid and 35 tons of sulfuric acid calculated as 60° Bé. It would require 19.5 tons of chlorine to make 37 tons of sulfuryl chloride. In other words, this Glover tower would make nearly one and a half times as much sulfuric acid as the entire chamber plant of which it was but a part; and at the same time would convert the total output of a very large chlorine plant into hydrochloric acid.

A smaller tower of the same height but 0.92 meter (3 feet) in diameter would produce, per 24 hours, 3.6 tons of 22° Bé. hydrochloric acid and 2.2 tons of sulfuric acid calculated as 60° Bé.

In order to produce 66° Bé. sulfuric acid it would probably be necessary to instal a small concentrating unit. Although the thermochemical data show that the hydrolysis of sulfuryl chloride gives out enough heat to raise the temperature of the acid in the bottom of the tower far above the boiling point of 66° Bé. sulfuric acid, it must not be forgotten that the hydrolysis proceeds very slowly in the strong acid. Consequently, it would probably be advisable to use the bottom of the hydrolyzing tower as a condenser for the concentrating unit. After starting, the concentrating unit would have

[11] Lunge, "Sulfuric Acid and Alkali," Vol. I, 1913, p. 878.

little work to do. As alternatives it might be possible to heat the bottom of the hydrolyzing tower directly with an oil burner, as in a tower concentrator, or indirectly with highly superheated steam.

The greater part of the sulfuric acid mist can be removed by the scrubbing action of the dilute acid condensed in the top of the tower. This would produce hydrochloric acid of about the same degree of purity as is found in the market at the present time. If a still higher purity is desired, it can be readily obtained by removal of the mist by electrical precipitation.

Finally, it should be pointed out that this new process falls in line with the modern tendency to change plants and processes to conform with the fundamental principles of industrial hygiene. Charles F. McKenna, in a report of the New York State Division of Industrial Hygiene,[12] says, "One of the dangers in the manufacture of hydrochloric acid is the annoying fumes which come from the hot salt cake when it is drawn from the furnace * * * the fumes of acid quickly cause the teeth to rot away." The manufacture of hydrochloric acid from sulfuryl chloride can be carried out entirely in closed apparatus, thus eliminating the discharge of these corrosive gases into the atmosphere.

[12] New York State Department of Labor, 2nd Report of the Factory Investigating Commission, **2**, 1067 (1913).

VITA

Carroll M. Salls was born in Burlington, Vermont on Dec. 19, 1893. He obtained his primary and collegiate training in that city receiving the degree of Bachelor of Science in Chemistry from the University of Vermont in 1916. He has been employed in the research and control laboratories of the Miller Rubber Co., Akron, O.; and in the works laboratory of the starch and glucose factory of the Canada Starch Co., Cardinal, Ontario. With the Canadian Explosives, Ltd., Montreal, he assisted in the development of the Naphtha Process from a Buchner funnel through two semi-commercial stages to a plant purifying 600,000 pounds of TNT per month, holding the position of Night Superintendent of this plant.

For the same explosives company, he installed and put into operation apparatus to make 50 tons of neutral sodium sulfite per month. On the same plant, he has also carried out research work on acids, dynamites, and black powder.

From August, 1919 to August, 1920 he was employed by the Rollin Chemical Corpn., Charleston, W. Va., for research work at McGill University, Montreal, on the chlorination of methane.

He was elected to Sigma XI by the Columbia Chapter in 1922.

During the college year 1922–23 he enjoyed the substantial honor of the Goldschmidt Fellowship.

From May, 1923 to Feb., 1924 he was assistant to Professor Ralph H. McKee in consulting practice, patent litigations, etc.

Then he entered the New York State Department of Labor, Division of Industrial Hygiene, for duty in the factories of New York State to carry out special investigations concerning the discharge of injurious dusts, fumes, and gases into the atmosphere. He has written a number of articles on constructive industrial hygiene, among which are two papers on recent hygienic improvements in the electrolytic alkali and chlorine industry.